

The study of metal sulphide nanomaterials obtained by chemical bath deposition and hot-injection technique

E.V. Maraeva¹, O.A. Alexandrova¹, N.A. Forostyanaya², V.S. Levitskiy¹, D.S. Mazing¹, L.N. Maskaeva², V.Ph. Markov², V.A. Moshnikov^{1,3}, A.A. Shupta¹, Yu.M. Spivak¹, S.S. Tulenin²,

¹ Saint Petersburg Electrotechnical University "LETI", ul. Prof. Popova, 5, 197376, Saint Petersburg, Russia

² Ural Federal University, ul. Mira, 19, 620002, Ekaterinburg, Russia

³ Peter the Great St.Petersburg Polytechnic University, 29, Polytechnicheskaya st., 195251, St.Petersburg, Russia

E-mail: jenvmar@mail.ru

Abstract. In this study lead sulphide – cadmium sulphide based layers were obtained through chemical deposition of water solutions and cadmium sulphide quantum dots were formed through hot-injection technique. The article discusses the results of surface investigations with the use of atomic force microscopy, Raman spectroscopy and photoluminescence measurements.

1. Introduction

Currently, the technology of chemical bath deposition of films of metallic sulphides [1-4] is especially attractive as far as such method of synthesis is relatively simple from technological point of view and effective at the same time; in comparison with vacuum thermal evaporation [5-8] it does not require expensive equipment. Microcrystalline layers of PbS – CdS solid solutions are traditionally used in infrared (IR) photosensitive devices and IR LEDs, operating at room temperature in 1 – 5 μm region. Increasing of cadmium concentration in a solid solution leads to increasing of bandgap energy. In nanoparticles with diameter reducing quantum-dimensional effects take place. An effective energy gap between discrete levels increases with nanoparticle's diameter reducing. Lead chalcogenides, as narrow-bandgap structures, are perspective materials as far as they can operate in IR region as well as in visible region depending on their diameters.

In this study the aspects of obtaining nanoparticles of lead chalcogenides and solid solutions via two various methods (chemical bath deposition, hot-injection technique) are researched, and its characterization with the use of such methods as atomic force microscopy (AFM), Raman spectroscopy and photoluminescence measurements is discussed.

1. Experiment

In this study lead sulphide – cadmium sulphide based layers were obtained through chemical bath deposition of water solutions using the following precursors: lead acetate $\text{Pb}(\text{CH}_3\text{COO})_2$; sodium



citrate Na_3Cit ; cadmium chloride CdCl_2 ; thiourea $(\text{NH}_2)_2\text{CS}$. The pH level was adjusted by adding water solution of ammonia NH_4OH . The volumes of solutions and volume of water added into reactor were calculated according to law of mass action depending on expected content of cadmium sulphide in the solid solution. Deposition was made on the vitroc ceramic-based substrate within 2 hours at temperature of 80°C . Ethylenediaminetetraacetic acid (ADTA) was used for oxide phases etching.

Cadmium sulfide nanocrystals were synthesized using hot-injection technique in non-polar medium of octadecene (ODE). Cadmium precursor solution was prepared by dissolving of cadmium oxide in mixture ODE and oleic acid in tree neck flask under nitrogen flow which resulted in formation of cadmium oleate solution. The second precursor solution which consisted of sulfur powder dissolved in ODE was quickly injected in the cadmium precursor solution under intensive stirring using glass syringe. This resulted in rapid nucleation of CdS nuclei with subsequent growth. Thus prepared nanocrystals has hydrophobic surface due to layer of stabilizing oleic acid.

AFM experiments were performed using NTEGRA-Therma nanolaboratory (NT-MDT, Zelenograd, Russia). Commercial etched silicon tips NSG 01 (NT-MDT, Zelenograd, Russia) with typical resonance frequency of 150 kHz were used as AFM probes.

Absorption spectra were acquired on a PE-5400UV UV-vis spectrophotometer (LLC "Ekohim"). Photoluminescence measurements were carried out on equipment based on fast scanning spectrometer Ocean Optics USB-4000 using laser excitation on $\lambda = 405 \text{ nm}$. The Raman spectroscopy was carried out with spectrometer LabRam HR800.

2. Results and discussion

As a result, a set of samples of solid solutions with different contents of cadmium sulphide was obtained, and properties of their surface were examined by analyzing the substrate area. The layers obtained were 100 to 500 nm thick depending on the original mix proportion. Regardless the proportion in original mix of solutions the most homogeneous film was formed in the center of substrate.

Figure 1 presents AFM images of lateral forces of obtained layers. The investigation of lead sulphide discovered that some crystallites consist of a number of nanolayers (figure 1a). By analysing of various scan areas it was determined that each layer thickness is about 40 nm.

According to [7, 8], when lead chalcogenides interact with oxygen the forming of oxygen phases takes place. In case of lead sulphide these phases are lead sulphate PbSO_4 , oxysulphate $\text{PbO} \cdot \text{PbSO}_4$. Its formation takes place even in normal conditions. For more detailed surface investigation the samples were etched in ethylenediaminetetraacetic acid (ADTA). Figures 1b,c present AFM images of layers being obtained from water solutions with cadmium (b) and without adding cadmium (c) after etching.

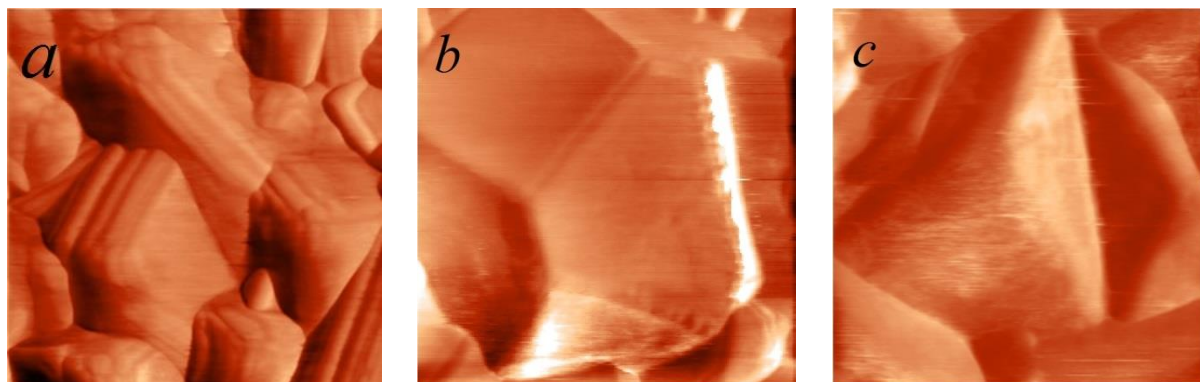


Figure 1. AFM image of lateral forces of PbS layer before etching (a), layers being obtained with cadmium (b) and without adding cadmium (c) after etching (scan size area is $1 \times 1 \mu\text{m}$)

It was determined that if cadmium was added into solution, crystallites with hexagonal structure were formed. In case of undiluted lead sulphide the crystallites had cubic or pyramidal form.

The Raman spectra were obtained in the backscattering geometry at room temperature with the spectrometer LabRamHR800 combined with a confocal microscope (manufactured by Jobin-YvonHoriba). The second harmonic of Nd:YAG-laser (wavelength 532 nm) served as the excitation source. The laser beam was focused to a spot with $\sim 1\text{-}2\text{ }\mu\text{m}$ diameter on the sample surface. Typical power density was lower 5 kW/cm^2 to avoid the influence of laser irradiation on the structure of the studied objects.

For Raman spectroscopy the films obtained with the use of solution with various concentration proportions of $\text{Pb}(\text{CH}_3\text{COO})_2$ and CdCl_2 in original mix were chosen. The concentration proportions of $\text{Pb}(\text{CH}_3\text{COO})_2$ and CdCl_2 in initial solution are reflected in Table 1.

Table 1. Concentration proportions of $\text{Pb}(\text{CH}_3\text{COO})_2$ and CdCl_2 in initial solutions

Sample	$[\text{CdCl}_2]/[\text{Pb}(\text{CH}_3\text{COO})_2]$
1	2.7
2	2
3	1
4	0.5
5	0

Figure 2 shows the Raman spectra of Samples 1, 2 and 3 standardised to the maximum intensity (a) and the spectra of Samples 1, 2 and 3 in the first order oscillation area of LO phonon (b).

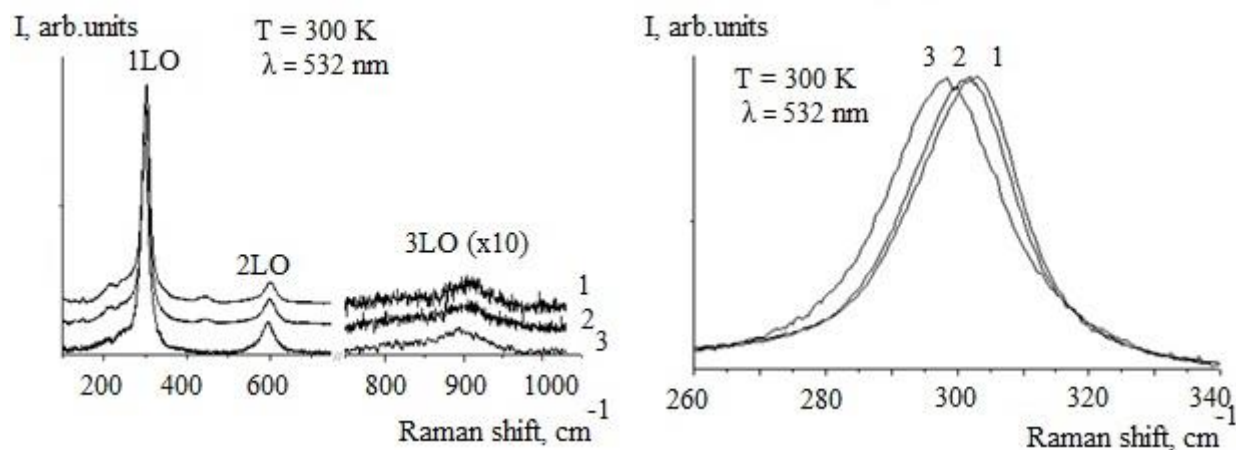


Figure 2. Raman spectra: 1 – sample 1; 2 – sample 2; 3 – sample 3

The Raman spectra of the samples are presented by broad bands with the maxima near 300 cm^{-1} , 600 cm^{-1} and 900 cm^{-1} (figure 2a). These bands are connected to multi-overtones with the longitudinal optical (LO) phonon mode CdS [9, 10]. As it was shown in [11-13], the most informative way to describe the features of the material's structural specifications is to analyse the position of the maximum of the first order LO phonon.

As it can be seen from the figure 2b, the positions of the band's maxima are different. Table 2 compares the positions of the maxima of 1LO phonon for these samples with single-crystal sample taken from the paper [14].

Table 2. Raman shifts for 1LO-phonons in CdS

Sample	Raman reflex maximum, cm^{-1}
Single crystal [11]	305
1	303
2	301
3	298

From the data presented in Table 2 it can be seen that the smallest shift is in the Raman spectra for Sample 1. An increased shift in the position of the maximum 1LO phonon is seen for samples containing Pb. From the data presented in Table 2, it is clear that in case of increase in the lead content of the resulting film there is an increase in the 1LO band shift. Apparently, this indicates an increase in the structural deformation of the CdS lattice due to the Pb atoms embedded there in.

Figure 3a shows the Raman spectra of samples 4 and 5, figure 3b shows the Raman spectra of Sample 4 before and after laser annealing at the power density ~ 4 times greater than used to obtain the Raman spectra. The same figure provides the spectrum of Sample 1 as an example (CdS).

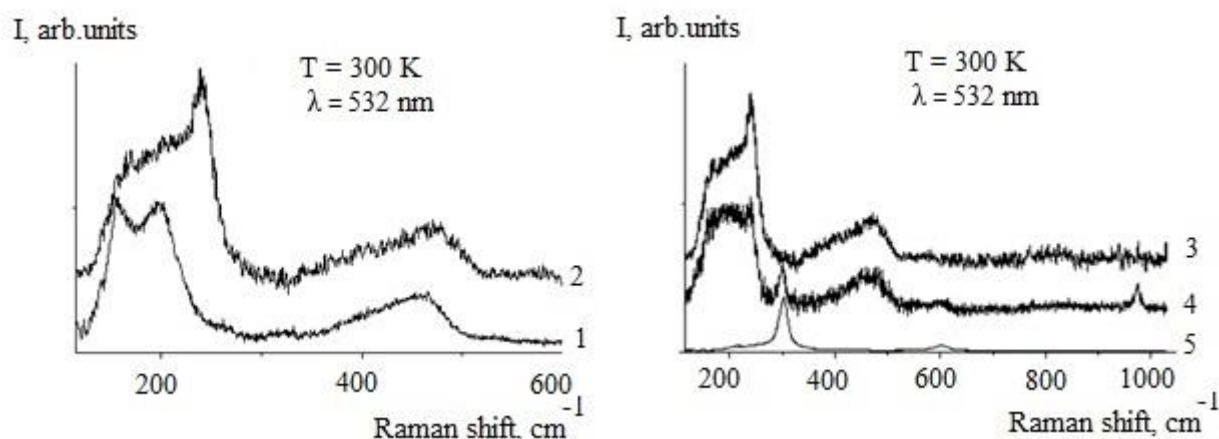


Figure 3. Raman spectra: 1 – sample 5; 2 – sample 4; 3 – sample 4 before laser heating; 4 – sample 4 after laser heating; 5 – sample 1

As it can be seen from the figure 3a, the Raman spectrum of Sample 5 is represented by three bands with the maximum positions near 150 cm^{-1} , 200 cm^{-1} и 440 cm^{-1} . This spectrum is very similar to the spectrum Pb^{34}S from [15]. The Raman spectrum of Sample 4 is significantly different from the spectra of all samples reviewed in this study. As it can be seen from the figure, in this spectrum there is an intense line with the position of the maximum near 250 cm^{-1} . However, the rest of the spectrum is close to the PbS spectrum. In the CdS spectra the maximum position of 1LO phonon is $\sim 300 \text{ cm}^{-1}$, so the band shift at $\sim 50 \text{ cm}^{-1}$ can be explained only by formation the solid solution $\text{Pb}_y\text{Cd}_{1-y}\text{S}$.

As it can be seen from the figure 3b, the additional bands appeared after laser annealing in the spectra of Sample 3 with peaks close to 300 cm^{-1} , 600 cm^{-1} and 970 cm^{-1} . As mentioned earlier, the bands with maxima near 300 cm^{-1} и 600 cm^{-1} are typical of the first and second order of CdS LO phonon. Some researchers attribute the appearance of a band with a maximum near 970 cm^{-1} to the formation of the PbS oxide phases [16]. It can also be noted that the intensity of the band with $\sim 250 \text{ cm}^{-1}$ maximum position has notably decreased after annealing, but the position of band's maximum remained unchanged. The constant position of the band maximum and the reduced intensity indicate

the quantitative reduction of $\text{Pb}_y\text{Cd}_{1-y}\text{S}$ phase, while the phase composition of this compound is preserved. Apparently, the annealing results in selection of the CdS phase from $\text{Pb}_y\text{Cd}_{1-y}\text{S}$ compound, as well as formation of PbS oxide phases.

Absorption and photoluminescence spectra of CdS nanocrystals prepared by means of hot injection method are presented in figure 4. Absorption band is blue shifted relative to what is expected for bulk CdS which indicates that nanocrystals are in the quantum confinement regime. As can be seen from spectra good monodispersity may be achieved using this approach as full width at half maximum parameter of photoluminescence peak is about 30 nm.

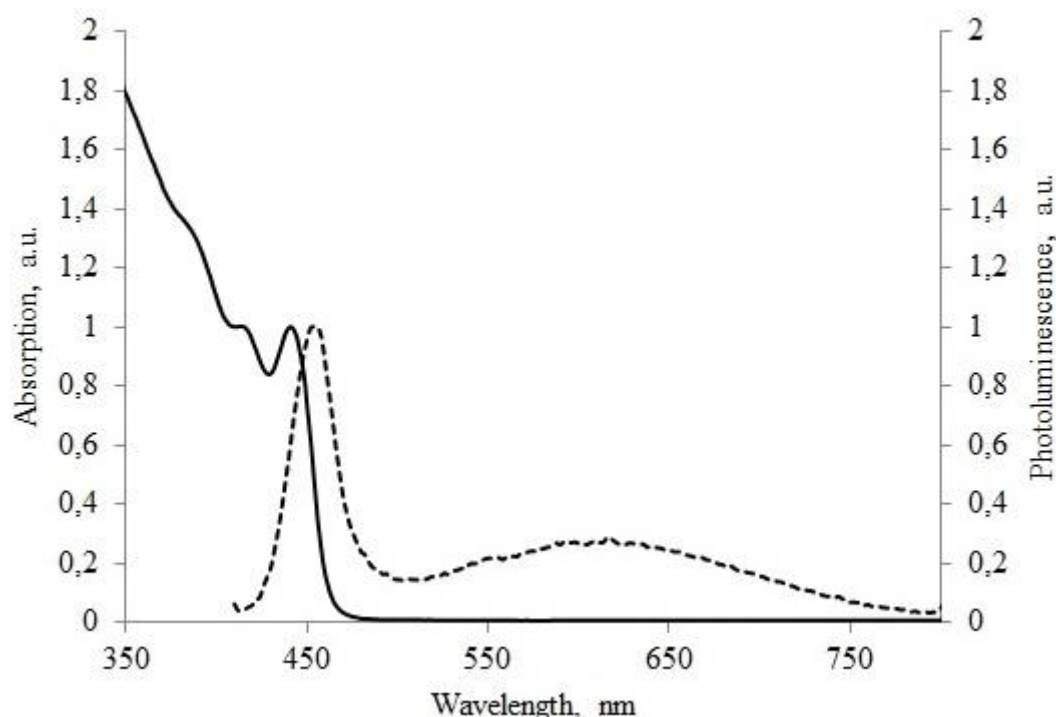


Figure 4. Absorption (full line) and photoluminescence spectra of colloidal CdS nanocrystals

Photoluminescence spectrum consists of two bands. The first one corresponds to interband transitions and reflects nanoparticle size distribution. The second one, of lower energy, is much broader and is associated with luminescence via trap states present within bandgap due to insufficient passivation of dangling bonds on nanocrystal surface. The mean size of nanocrystals was estimated to be approximately 4.8 nm. This assessment was made using equation from the work [17] which describes experimental correlation between nanocrystal size and wavelength of the first excitonic peak in absorption spectrum.

Conclusions

The paper discusses the aspects of obtaining lead sulphide – cadmium sulphide layers and cadmium sulphide quantum dots. The surface layers morphology are studied with the use of atomic force microscopy. AFM measurements after oxygen phases etching discovered that in case of adding cadmium into solution crystallites with hexagonal structure are formed. In case of undiluted lead sulphide the crystallites have cubic or pyramidal form. AFM data has a good correlation with the results of Raman spectroscopy.

Cadmium sulfide nanocrystals are synthesized using hot-injection technique and its absorption and photoluminescence spectra are studied. The results discussed are perspective for using in optoelectronics and for formation biological and medicinal markers for cellular structure studying.

Acknowledgments

The reported study was supported by grant of Russian Science Fund (project №14-15-00324) (a part of the study involving AFM investigation, quantum dots obtaining) and also by program 211 of Russian Federation Government № 02. A 03.21.0006 (a part of the study involving layers obtaining with the use of chemical bath deposition).

References

- [1] Markov V, Maskayeva L, Ivanov P 2006 *Hydrochemical deposition of metallic sulphide films: simulation and experiment* (Ekaterinburg)
- [2] Markov V F, Maskayeva L N, Kitaev G A 2000 *Inorganic Materials* **36** 1194
- [3] Markov V F, Maskayeva L N 2010 *Russian Journal of Physical Chemistry A*. **84** 1288
- [4] Katysheva A S, Markov V F, Maskayeva L N 2013 *Russian Journal of Inorganic Chemistry* **58** 833
- [5] Chesnokova D B, Moshnikov V A, Gamarts A E, Maraeva E V, Aleksandrova O A, Kuznetsov V V 2010 *Journal of Non-Crystalline Solids* **356** 2010
- [6] Moshnikov V A, Gamarts A E, Chesnokova D B, Maraeva E V 2011 *Inorganic Materials*. **47** 18
- [7] Maraeva E V, Moshnikov V A, Tairov Y M 2013 *Semiconductors* **47** 1422
- [8] Golubchenko N V, Moshnikov V A, Chesnokova D B 2006 *Glass Physics And Chemistry* **3** 337
- [9] Leite R C C, Porto S P S 1966 *Phys. Rev.* **17** 10
- [10] Chuu D S, Dai C M, Hsieh W F, Tsai C T 1991 *J. Appl. Phys.* **69** 8402
- [11] Oladeji I O, Chow L, Liu J R, Chu W K., Bustamante A N P, Fredricksen C, Schulte A F. 2000 *Thin Solid Films* **359** 154
- [12] Balandin A, Wang K L, Kouklin N, Bandyopadhyay S 2000 *Appl. Phys. Lett.* **76** 137
- [13] Prabhu R R, Khadar M A 2008 *Bull. Mater. Sci.* **31** 511
- [14] De Mello O., Hernandez L, Zeleya-Angel O, Lozada-Morales R, Becerril M, Vasco E 1994 *Appl. Phys. Lett.* **65** 1278.
- [15] Sherwina R, Clark R J H., Lauck R, Cardona M 2015 *Solid State Communications* **134** 565
- [16] Pérez R G, Téllez G H, Rosas U P, Torres A. M, Tecorralco J H, Lima L C and Moreno O P 2013 *Journal of Materials Science and Engineering* **3** 1
- [17] Yu W W, Qu L H, Guo W Z and Peng X G 2003 *Chem. Mater.* **15** 2854